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Anion-Exchange Chromatographic Separation of Hg for Isotope Ratio Measurements by Multicollector ICPMS

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A procedure is described for precise Hg isotope ratio measurements by solution nebulization multicollector inductively coupled plasma mass spectrometry (MC-ICPMS). Hg was released from geological samples using aqua regia extraction and then separated from other matrix elements with the aid of anion-exchange chromatography using strongly basic Dowex 1-X8 anion-exchange resin. Performance of the chromatographic procedure was evaluated using various types of replacement anions for elution of mercury, including L-cysteine, thiourea, NO₃⁻, and SO₄²⁻. A solution of 0.15% L-cysteine in 0.06 M HCl was found to be the most convenient eluent for subsequent MC-ICPMS measurements. The optimized procedure provides separation of Hg from virtually all concomitant matrix elements while maintaining quantitative (>95%) recovery. In addition, band displacement chromatographic experiments were conducted to assess whether the anion-exchange purification can produce Hg isotope fractionation artifacts. No isotope fractionation between the Hg(II)-L-cysteine complex in aqueous solution and Hg ions in the anion-exchange resin was observed. Hg isotope ratio measurements were performed using the bracketing standards approach and on-line correction for instrumental mass discrimination using TI spiking and normalization to the ²⁰⁵Tl/²⁰³Tl ratio. The absence of spectral interference during Hg isotope ratio measurements was verified using a three-isotope plot. Uncertainties of Hg isotope ratio measurements for replication of the entire procedure, expressed as two standard deviations, are better than $\pm 0.08\%$ /amu. The described procedure facilitates study of variations in the isotopic composition of Hg in nature.

Mercury has seven naturally occurring isotopes, namely, ¹⁹⁶-Hg, ¹⁹⁸Hg, ¹⁹⁹Hg, ²⁰⁰Hg, ²⁰¹Hg, ²⁰²Hg, and ²⁰⁴Hg, with relative abundances ranging from 0.15 to 29.9%.¹ Recent published data from several research groups have demonstrated per mil level variations of the Hg isotopic composition in both natural samples and laboratory experiments.²⁻¹¹ These authors suggested that variations in the isotopic composition of Hg can be used as tracers to study a wide variety of chemical and biological processes in nature. High-precision measurements of Hg isotope ratios are now made exclusively by multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS), precision of which is superior to that of both thermal ionization mass spectrometry and singlecollector ICPMS. It is interesting to note that all published measurements of Hg isotope ratios by MC-ICPMS made to date have been performed using on-line cold vapor generation as a sample introduction technique. Considering the high volatility of Hg, vapor generation is a straightforward means of releasing Hg from samples. Liquid samples can be analyzed by reducing the Hg ions in solution and aerating inert gas through the liquid to liberate elemental Hg into the gas phase. Similarly, solid samples can be digested followed by reduction and liberation of Hg⁰ from the solution. Vapor generation methods offer such clear advantages as high sensitivity and separation of the matrix. However, for certain types of samples, vapor generation has some drawbacks. Most significant of them is that complexing agents, e.g., inorganic anions such as Cl-, I-, CN-, and Br-,12,13 organic complexes,^{14,15} and oxidizing substances¹³ present in the sample solution, can interfere with reduction of Hg leaving a fraction of the element in solution as Hg²⁺. It has been shown that Hg isotope fractionation occurs during reduction of the element from Hg²⁺ to Hg^{0,11} Hence, there is a risk of bias in isotopic data if Hg liberation from solution is incomplete. In addition, on-line vapor

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generation requires special devices for simultaneous vaporization of Hg and introduction of nonvolatile internal standard (TI).

The points raised above do not discourage cold vapor generation as a very useful sample introduction technique for analysis of Hg at low concentrations in particular but suggest that an alternative, solution nebulization MC-ICPMS, is worthy of closer examination. This is particularly true considering the reported progress made in controlling Hg memory effects during measurements with inductively coupled plasma instruments.^{16–18} The latter was thought to be a serious issue in earlier attempts to achieve precise Hg isotope analysis.¹⁹

Successful use of solution nebulization MC-ICPMS requires separation of Hg from the concomitant matrix.^{20,21} Ion-exchange chromatography is a most effective and commonly used method for this purpose. There are numerous studies devoted to use of ion-exchange chromatography for separation of various chemical forms of Hg,²²⁻²⁵ but to the best knowledge of the authors, there is no study that discusses application of ion-exchange chromatography to separation of Hg for subsequent isotopic analysis by MC-ICPMS. In this work, an anion-exchange chromatographic separation of Hg for isotope ratio measurements by solution nebulization MC-ICPMS has been developed. Performance of the chromatographic procedure was evaluated by using a number of eluents for Hg including L-cysteine, thiourea, and nitric and sulfuric acids. Chromatographic conditions ensuring efficient separation and quantitative recovery of Hg have been established. We also performed band displacement chromatographic experiments to assess potential Hg isotope fractionation between the Hg(II)-L-cysteine complex in the solution and Hg(II) ions on the anionexchange resin.

EXPERIMENTAL SECTION

Apparatus and Reagents. Glass Pasteur pipets (3-mL volume) were fitted with plugs of quartz wool at their outlets and filled with ~0.8 mL of resin to produce ~4 cm long \times 0.5 cm i.d. chromatographic columns. The resin used in this study was a strongly basic anion-exchange resin Dowex 1-X8, 100–200 mesh (J.T. Baker Chem. Co., Phillipsburg, NJ). High-purity deionized water was obtained from a NanoPure mixed bed ion-exchange system fed with reverse osmosis domestic feedwater (Barnstead/ Thermolyne Corp.). Hydrochloric and nitric acids were purified in-house by sub-boiling distillation of reagent grade feedstock using a quartz still. A 0.2 M BrCl solution was prepared in a fume hood by dissolving 27 g g of KBr (Fisher Scientific, Nepean, Canada) in 2.5 L of HCl and then slowly adding 38 g of KBrO₃ while stirring. Analytical-reagent grade NaOH, thiourea, and L-cysteine (Merck, Darmstadt, Germany) were used as supplied.

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Table 1. Hg Separation Sequence for Anion-Exchange Chromatography Using 0.8 mL of 100–200 Mesh Strongly Basic Dowex 1-X8 Resin

eluent	vol (mL)	purpose
4 M HNO ₃	10	resin cleaning
2 M HCI 2 M HCI/1 M HNO ₃	$\frac{6}{20}$	sample load
1 M HCl	10	matrix elution
0.15% L-cysteine/0.06 M HCl	10	Hg elution

All calibration and internal standard solutions used were prepared by diluting single-element standard solutions (SCP Science, Québec, Canada).

Sample Preparation. Hg was released from samples using the procedure modified from Smith.²⁶ The samples were weighed into capped PFA containers and digested with 5 mL of aqua regia (3:1 mixture of 12 M HCl and 16 M HNO₃) on a heating block at \sim 100 °C for 1 h. After the samples had cooled to ambient temperature, they were poured into precleaned polyethylene centrifuge vials and centrifuged at 5000 rpm for 4 min to separate solid residue from solution. The solutions were decanted into another precleaned vial and diluted 5-fold with MQ-water. These solutions were then loaded onto the anion-exchange columns.

Chromatographic Procedures. The columns were cleaned with 10 mL of 4 M HNO₃ for the purpose of cleaning and regenerated to the chloride form with 6 mL of 2 M HCl. Further details of sample loading and elution of Hg are shown in Table 1. Recovery of Hg was checked for each sample by ICPMS measurements on aliquots taken before and after chromatographic separation.

Longer chromatographic columns, \sim 30 cm long \times 0.8 cm i.d., were used in band displacement chromatographic experiments. During the experiments, the effluent flowing out of the column was collected in small fractions, which were subsequently analyzed by ICPMS and MC-ICPMS for Hg concentration and isotope ratio measurements, respectively. Parameters such as concentrations of L-cysteine and thiourea in the eluting solutions and length of the chromatographic columns were varied in order to assess Hg isotope fractionation between Hg in the solution and Hg in the anion-exchange resin. Total procedural blanks were prepared for all sample manipulations and found to contain negligible quantities of Hg (<5 ng) relative to those of Hg in samples. As the samples investigated here contained relatively elevated levels of total mercury, this level of blank was deemed to be quite acceptable. It is recognized that a more careful selection of container surfaces and cleaning of reagents may be required to reduce the blank to levels needed when studies are conducted on natural materials containing only 10–20 ng total mercury.

Mass Spectrometric Measurements. Prior to MC-ICPMS measurements, the concentrations of Hg in the samples were determined by quadrupole ICPMS using an Elan 6000 (Perkin-Elmer Sciex, Thornhill, ON, Canada). No significant Hg memory effect was observed when using 0.12 M HCl/0.002 M HBr solution as sample matrix and wash solution; the Hg signal (>2.5 × 10⁶ counts/s) was reduced to its baseline level (~4 × 10² counts/s) within several minutes of washing. After the concentration of Hg

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Table 2. Typical Operating Conditions for the Neptune MC-ICPMS during This Study

rf power	1250				
sampler and skimmer cones	nickel, 1.1- and 0.8-mm orifice diameter, respectively				
argon gas flow rate (l/min):					
coolant	16				
auxiliary	0.8				
nebulizer	\sim 1.1 (optimized before each measurement session)				
sample uptake rate (mL/min)	~ 0.05				
mass resolution	~ 400				
Ion lens settings	optimized for maximum intensity of Hg signal				
²⁰² Hg sensitivity	6 V/mg l ⁻¹				

had been determined, the samples were appropriately diluted with 0.12 M HCl/0.002 M HBr to match Hg concentrations in the standards, spiked with Tl for instrumental mass discrimination correction at 1/8 of the Hg concentration to match the intensities of ²⁰²Hg⁺ and ²⁰⁵Tl⁺ signals and then subjected to isotope ratio measurements using Neptune MC-ICPMS (Thermo Finnigan, Bremen, Germany). Typical operating conditions for the instrument are given in Table 2. Low-resolution mode was used in this study with $R_{\text{power}(5,95\%)} \sim 400$. Samples and standards were introduced into the plasma in self-aspiration mode through a stable introduction system (Thermo Finnigan) consisting of tandem quartz spray chamber arrangements (cyclone + Scott doublepass), a microconcentric PFA nebulizer, and a peristaltic pump (Perimax 12, Spetec, Erding, Germany). Instrument tuning and optimization of signal intensity were performed before each measurement session. The measurements were conducted in the static mode. 198Hg, 199Hg, 200Hg, 201Hg, 202Hg, 203Tl, and 205Tl isotopes were collected by Faraday cups at low 3, low 2, low 1, central, high 1, high 2, and high 3 positions, respectively. Each sample measurement consisted of 7 blocks, each block comprising 10 cycles of ~4.2-s duration. The analytical routine does not include baseline (on peak zero) correction. To avoid memory effects from previous solutions, ~ 5 min of signal stabilization was allowed before starting the measuring sequence. It was observed that 201 Hg signal of 1.0 V dropped to the blank level of ~ 0.01 V within 60 s of washing by 0.12 M HCl/0.002 M HBr solution. All analyses were made in a sequence of isotope standard, two "unknown" samples, isotope standard, and so on. Measuring two samples in between the bracketing standards were observed not to degrade the external precision. Standard Reference Material NIST-3133 (Hg standard solution, Lot No. 991304) was used as the isotopic standard in this work. The concentrations of samples and bracketing standards were matched to within 20%. The typical sensitivity for ²⁰²Hg was ~6 V mg⁻¹ L⁻¹. Typical concentration of Hg in the samples measured by MC-ICPMS was 0.25 ppm. An exponential model for correction of instrumental mass discrimination was used, as described elsewhere.27

The on-line data processing included calculation of the raw ratios and filtering of outliers by a $2-\sigma$ test. Further statistical treatment of the data was performed off-line. Results for the isotopic analyses of Hg in sediments are expressed in the

 δ -notation, as defined by the relationship

$$\delta^{X/198} \text{Hg} = \left[\frac{({}^{X}\text{Hg}/{}^{198}\text{Hg})_{\text{sample}}}{({}^{X}\text{Hg}/{}^{198}\text{Hg})_{\text{standard}}} - 1 \right] \times 1000\% \quad (1)$$

where ^{*X*}Hg is ¹⁹⁹Hg, ²⁰⁰Hg, ²⁰¹Hg, and ²⁰²Hg isotope, respectively, in the measured ratios for sample and standard, corrected for instrumental mass discrimination using Tl (205 Tl/ 203 Tl = 2.3875).

RESULTS AND DISCUSSION

Performance of Anion-Exchange Chromatography. Due to its importance in analytical chemistry, the Dowex 1-X8 resin has been widely studied.^{22,28-31} The resin is a strongly basic anion exchanger with a styrene divinylbenzene polymer skeleton to which tertiary ammonium groups have been linked. Dowex 1-X8 exhibits a high selectivity for chloroanionic complexes of Hg. The sample solutions were loaded onto the columns in ~1.8 M HCl/ 0.8 M HNO₃ solution. The dominant chemical form of Hg in this solution is presumably chloroanionic HgCl₃⁻ and HgCl₄²⁻ complexes,²² which efficiently exchange with Cl⁻ on the resin. In contrast, the concentration of 2 M HCl in sample matrixes is not sufficient for formation of an FeCl4⁻ complex,^{30,32} which otherwise could be a serious interfering species for Hg, because Fe is a major constituent of sedimentary material. Elution of concomitant matrix elements coadsorbed with Hg, such as Mo, Zn, Cu, and Cd, was realized by using 10 mL of 1 M HCl. Hg adsorbed on the resin remains unaffected by subsequent elutions with HCl because it is very strongly adsorbed on the anion-exchange resin from HCl media at concentrations ranging from 0.001 to 12 M.²² Hg was eluted from the column with 10 mL of 0.15% L-cysteine/0.06 M HCl solution. The strong preference of Hg(II) for the thiol group is well-known, although conflicting overall formation constants for Hg-L-cysteine complexes have been reported, ranging from 8 to 62 in terms of log β .^{33,34} The kinetics of extraction of Hg from the resin was observed to be fast offering a possibility of decreasing the elution volume for Hg. More than 80% of the element is eluted with the first 2 mL of the 0.15% L-cysteine/0.06 M HCl solution.

Confirmation that the yield of Hg from the separation process is quantitative is important in light of a known fact that ionexchange chromatography can lead to fractionation of the isotopic composition of elements.^{21,30} For the anion-exchange procedure described above, a recovery of >95% from the sediment material studied was achieved, and so any fractionation effects observed can be entirely ascribed to the samples. The absence of artificially introduced isotopic fractionation of Hg due to its incomplete recovery after the anion-exchange chromatography was also confirmed by replicated processing of both the Hg standard and sediment samples through the anion-exchange purification procedure and measurements of its Hg isotopic composition by MC-ICPMS.

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Table 3. Some Performance Characteristics of Solutions Used for Elution of Hg in Anion-Exchange Chromatography Based on Replicate Processing of Sediment Reference Material PACS-2 ($n \ge 3$)

solution ^a	recovery of Hg, %	shortcomings of use as a matrix component for isotope analysis by MC-ICPMS
0.15% L-cysteine/0.06 M HCl 0.2% thiourea/0.06 M HCl 0.5% $\rm H_2SO_4$	>95 >95 >90	no shortcomings have been observed origin of systematic interference on ¹⁹⁸ Hg (i) dilution is required to minimize damage to sample/skimmer cones; (ii) white precipitate, presumably sulfate salt was observed upon overnight storage
4 M HNO ₃	from 55 to 75	dilution is required
Volume of the solution used for elution of	Hg is constant and equal to 10 m	I.

During initial stages of this work, we evaluated the performance of other eluents for Hg, including thiourea and nitric and sulfuric acids. Table 3 summarizes some results of these experiments and the shortcomings revealed using the aforementioned eluents relative to a solution of L-cysteine. In addition, to evaluate potential isotope fractionation of Hg during extraction of the element from the resin, band displacement chromatographic experiments were performed using both L-cysteine and thiourea as the eluents. Chromatography operated in the band displacement manner implies the following two conditions are satisfied.^{35,36} First, the isotopic chemical species to be separated is eluted through the column by a specific displacing eluent solution. Second, the rate of movement of the band through the column allows equilibrium to be established between chemical species in the solution phase and the resin phase. The latter condition was presumably satisfied by using 30-cm-long chromatographic columns and a slow (~0.15 mL/min) flow rate of the elution solutions. As shown in Figure 1, no Hg isotope fractionation is associated with displacing Hg ions from the resin by solutions of both 0.15% L-cysteine/0.06 M HCl and 0.15% thiourea/0.06 M HCl.

a J

Spectral Interferences. Although chemical separation of Hg from natural samples using anion-exchange chromatography has been widely applied,²² detailed investigations of the efficiency of removal of potentially interfering elements are lacking. Potential interfering ions on Hg and Tl isotopes can appear due to isobaric overlap from elements that could be present in the sample and from formation of refractory oxide and polyatomic ions during the process of measurement. Considering elemental concentrations, isotopic abundances, and conditions employed in this study, only polyatomic ion formation on ¹⁹⁸Hg is judged to present a potentially serious source of spectral interferences in the measurement of Hg isotope ratios. This is discussed in more detail below.

It is worth noting the possible formation of gold hydride (¹⁹⁷-Au¹H) and its interference on ¹⁹⁸Hg. This interference was observed during our trial experiments in which Au was added to solutions to stabilize Hg. It is interesting that Au has been used as both a trap and a stabilizing agent in solutions for isotope analysis of Hg by cold vapor generation MC-ICPMS;¹⁰ however, no spectral interference on ¹⁹⁸Hg was reported. This is presumably



Figure 1. Hg isotope compositions in elution fractions from chromatographic experiments (see text for details). Hg loaded onto the anion-exchange columns was identical to the Hg used as a standard in the mass spectrometric analysis. Hence, δ Hg per atomic mass unit of the loaded Hg is equal to zero. Open symbols represent the data from experiments using 0.2% thiourea/0.06 M HCl solution for elution of Hg; filled symbols display the data from experiments using 0.15% L-cysteine/0.06 M HCl solution for elution of Hg. Uncertainties on δ^{199} Hg/¹⁹⁸Hg are better than 0.08‰ at the level of two standard deviations.

in accord with the fact that no evaporation of Au occurs during the process of cold vapor generation. Blum and Bergquist¹⁰ also noted that separation of Au from Hg in the NIST standard gave better precision of Hg isotope ratio measurements that may be attributed to AuH interference.

Another interference on ¹⁹⁸Hg was observed from thiourea present in the solution matrix. This interference is attributed to a decomposition product of thiourea arising from the process of ionization. Interestingly, measurements of other Hg isotope ratios, including ¹⁹⁹Hg, ²⁰⁰Hg, ²⁰¹Hg, and ²⁰²Hg, are not affected by the presence of thiourea in solution as illustrated by three isotope plots in Figure 2. The description of these plots for the aforementioned Hg isotopes is given in detail below. The interferences originating from thiourea could not be resolved instrumentally even if high-resolution mode is used. This interference is the main reason why a thiourea solution was abandoned as an eluent for Hg during the anion-exchange procedure and replaced by Lcysteine. Data obtained in this study show that the presence of L-cysteine in solution did not result in formation of any interfering ions on the measured Hg and Tl isotopes.

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Figure 2. Three-isotope plot of (a) δ^{200} Hg/¹⁹⁸Hg vs δ^{202} Hg/¹⁹⁸Hg and (b) δ^{200} Hg/¹⁹⁸Hg vs δ^{201} Hg/¹⁹⁸H for replicate measurements of Hg standard solution and sediment samples (n = 61) constructed using the approach of Young et al.³⁷ (see text for details). Filled symbols are samples of PACS-2 sediments and synthetic samples; open symbols represent NIST 3133 standards. Uncertainty bars represent one standard deviation. Linear regression using weighting of both variables yielded the following intercept (a_w) and slope (b_w) estimates: (a) $a_w = 0.002 \pm 0.001$ and $b_w = 0.506 \pm 0.002$ (R = 0.999); (b) $a_w = 0.001 \pm 0.003$ and $b_w = 0.664 \pm 0.006$ (R = 0.997). Slopes for both plots of δ^{200} Hg/¹⁹⁸Hg vs 202 Hg/¹⁹⁸Hg are consistent with theoretical values of 0.505 and 0.670, respectively, for mass-dependent (equilibrium) fractionation process.

Among isobaric interference, ¹⁹⁸Pt is the only one of concern on the measured Hg isotopes (²⁰⁴Pb is not considered here because ²⁰⁴Hg was not determined). However, Pt was not present in detectable concentrations in any samples, either before or after anion exchange. The probability of spectral interference originating from refractory oxides (Os, Rh, W, Ta, Pt) is considered very low because most of these elements are present at trace level in environmental and geological samples and these are readily separated from Hg using the anion-exchange procedure.

Instrumental Mass Discrimination Correction. Under normal operating conditions, mass discrimination in the Hg region observed in this study was $\sim 2.0\%$ per atomic mass unit. An exponential model for its correction has been adopted using Tl as an internal dopant. A detailed description of the procedure can be found elsewhere.²⁷ Our data show that Tl possesses favorable characteristics for on-line mass discrimination correction of Hg isotope ratios. As seen in Figure 3 for ²⁰¹Hg/¹⁹⁸Hg and ¹⁹⁹Hg/¹⁹⁸. Hg plotted versus ²⁰⁵Tl/²⁰³Tl over measurement sessions from March to December 2007, despite the mass fractionation factors (×c4) for isotopes of Hg and Tl are not identical, their ratios produce well-defined linear arrays with $R^2 \sim 0.9$ (n = 61). Worth mentioning is that the levels of instrumental mass discrimination have been computed using abundances taken from SRM NIST 3133 certificate for Hg and the recent IUPAC data compilation¹ for Tl, the latter because no materials with absolute isotopic composition determined with sufficient precision are available for Tl. The IUPAC values do not necessarily represent the true isotopic composition of the standard solutions used here. Fortunately, for the purposes of drift correction and calculation of relative Hg isotope ratios, i.e., δ -values, this is of no consequence.

Three isotope plots can be applied for testing the effectiveness of the procedure for mass discrimination correction and absence



Figure 3. Relationship between fractionation coefficients (f): (a) $f(^{202}\text{Hg}/^{198}\text{Hg})$ vs $f(^{205}\text{TI}/^{203}\text{TI})$ and (b) $f(^{200}\text{Hg}/^{198}\text{Hg})$ vs $f(^{205}\text{TI}/^{203}\text{TI})$ during separate measurement sessions over March–August 2007 (n = 61). Open symbols represent isotope standards; filled symbols are samples of sediments and synthetic solutions purified using anion-exchange chromatography. Linear regression yields the equations: (a) y = 0.642x + 0.095 ($R^2 = 0.918$); (b) y = 0.68x + 0.122 ($R^2 = 0.903$). Note that slopes of regression fHg vs fTl to correct for mass discrimination were determined for each measurement session separately.

of spectral interferences on the measured isotopes provided that isotope ratios in the samples follow mass-dependent distribution. Hg isotope ratios in sediment reference material PACS-2 are expected to be mass-dependent and therefore were chosen as samples for plotting in three isotope space. The theoretical background for construction and use of three isotope plots has been elaborated in detail and described elsewhere.³⁷ Here we refer only to the necessary formulas needed in this work. In this approach, mass-dependent isotope fractionation laws for three isotopes, ¹⁹⁸Hg, ²⁰⁰Hg, and ²⁰¹Hg, can be formulated in the expression

$$\delta^{200/198} \operatorname{Hg} = \left[\left(\frac{1000 + \delta^{201/198} \operatorname{Hg}}{1000} \right)^{\beta} - 1 \right] \times 1000\% \quad (2)$$

where the exponent, β , takes different forms in the case of kinetic

$$\beta = \frac{\ln[m(^{198}\text{Hg})/m(^{200}\text{Hg})]}{\ln[m(^{198}\text{Hg})/m(^{201}\text{Hg})]} = 0.668$$
(3a)

$$\beta = \frac{\left[\frac{1}{m(^{198}\text{Hg})} - \frac{1}{m(^{200}\text{Hg})}\right]}{\left[\frac{1}{m(^{198}\text{Hg})} - \frac{1}{m(^{201}\text{Hg})}\right]} = 0.670$$
(3b)

control of the process governing isotopic fractionation.

As this relationship defines a nonlinear mass fractionation curve,³⁷ linearization of the array was employed prior to linear regression analysis using weighting of both variables³⁸

$$\delta^{X/198} \text{ Hg} = \ln \left[\frac{({}^{X}\text{Hg}/{}^{198}\text{Hg})_{\text{sample}}}{({}^{X}\text{Hg}/{}^{198}\text{Hg})_{\text{standard}}} \right] \times 1000\%$$
(4)

$$\delta'^{200/198}$$
Hg = $a_{\rm w} + b_{\rm w} \delta'^{201/198}$ Hg (5)

The weighted intercept obtained for repeated measurements of samples of sediments and synthetic solutions, $a_{\rm w} = (1.0 \pm 3.0) \times 10^{-3}$ (95% confidence interval, n = 61) is not statistically different from zero (Figure 2b). The weighted slope, $b_{\rm w} = 0.664 \pm 0.006$ ($R^2 = 0.996$), the experimental estimate of β , is statistically indistinguishable from that expected for mass-dependent isotope fractionation. This agreement indicates the robustness of the applied procedure for mass discrimination correction and the interference-free measurements of 200 Hg/ 198 Hg and 201 Hg/ 198 Hg ratios. However, uncertainty associated with the experimental estimate of β is too large to make inference on the control (kinetic or equilibrium) of isotopic fractionation for the measured samples. This uncertainty is attributed to nonideal separation of Hg from concomitant matrix elements.

Hg Isotope Ratio Measurements. The reproducibility of isotopic measurements of Hg has been assessed by repeated measurements of subsamples of sediment reference material PACS-2 over a period of 3 months (n = 14) as well as for replicate measurements of fish tissue reference materials DORM-2 and DOLT-3. Data for these materials are listed in Table 4 and show that the Hg concentrations in the sample digests determined here are concordant with the certified values. The long-term reproducibility has been evaluated as 0.06, 0.1, 0.14, and 0.18% for ¹⁹⁹Hg/ ¹⁹⁸Hg, ²⁰⁰Hg/¹⁹⁸Hg, ²⁰¹Hg/¹⁹⁸Hg, and ²⁰²Hg/¹⁹⁸Hg ratio measurements at the 95% level of confidence (2 standard deviations of the mean; n = 14). The aforementioned levels of precision are greater than those reported in Blum and Bergquist.¹⁰ Of note is that variations in Hg isotopic composition of synthetic mixtures derived from the NIST 3133 standard after separation by anion-exchange chromatography are also within the precision limits stated above. The long-term repeatability obtained above may therefore be regarded as an overall analytical precision.

An interesting observation is that Hg isotopic composition of two reference fish tissue standards (DORM-2 and DOLT-3) was found to be mass-independent. The likely cause of massindependent Hg isotope fractionation in fish tissues was discussed in a recent article by Blum and Berggquist.¹¹ These authors also reported Hg isotope data of DORM-2 reference material, which are in an excellent agreement with the data obtained in the present study.

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Fable 4. Hg Concentrations an	d Isotope Data	for Reference	Materials and S	Synthetic :	Samples Use	ed in This	s Study
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	$(\mu g g^{-1})$										
	found		contifical	$\delta^{199/198}$ Hg	CTD	$\delta^{200/198}$ Hg	CTD	$\delta^{201/198}$ Hg	CTD	$\delta^{202/198}$ Hg	CTD
sample	Iouna		cerulled	(%)	51D	(%)	51D	(%)	51D	(%0)	51D
PACS-2, mean	2.95 ± 0.13	5 3	3.04 ± 0.20	-0.07	0.03	-0.14	0.05	-0.21	0.07	-0.28	0.09
subsample 1	2.91			-0.09	0.03	-0.17	0.032	-0.28	0.03	-0.37	0.08
subsample 2	2.86			-0.12	0.02	-0.18	0.024	-0.30	0.02	-0.36	0.02
subsample 3	3.15			-0.11	0.04	-0.18	0.087	-0.28	0.10	-0.37	0.06
subsample 4	3.10			-0.08	0.04	-0.15	0.019	-0.23	0.02	-0.30	0.03
subsample 5	2.77			-0.07	0.01	-0.14	0.026	-0.21	0.03	-0.28	0.05
subsample 6	2.85			-0.03	0.01	-0.06	0.058	-0.08	0.06	-0.11	0.01
subsample 7	2.90			-0.10	0.01	-0.18	0.075	-0.25	0.09	-0.36	0.05
subsample 8	3.10			-0.09	0.01	-0.17	0.006	-0.26	0.01	-0.35	0.01
subsample 9	3.08			-0.07	0.01	-0.13	0.086	-0.20	0.09	-0.27	0.05
subsample 10	2.98			-0.06	0.03	-0.13	0.005	-0.19	0.00	-0.25	0.05
subsample 11	2.75			-0.07	0.05	-0.15	0.020	-0.22	0.02	-0.29	0.03
subsample 12	2.81			-0.02	0.03	-0.03	0.029	-0.06	0.03	-0.09	0.05
subsample 13	3.20			-0.06	0.01	-0.13	0.018	-0.19	0.02	-0.25	0.01
subsample 14	2.77			-0.07	0.01	-0.14	0.049	-0.23	0.05	-0.29	0.03
DOLT-3, mean	3.28 ± 0.06	6 3	3.37 ± 0.14	0.25	0.05	-0.70	0.04	-0.30	0.02	-1.26	0.05
subsample 1	3.23			0.29	0.01	-0.74	0.02	-0.32	0.02	-1.28	0.03
subsample 2	3.34	(0.06	0.25	0.03	-0.70	0.04	-0.28	0.04	-1.3	0.05
subsample 3	3.28	_ :	3.28	0.2	0.02	-0.67	0.05	-0.31	0.04	-1.2	0.04
DORM-2, mean	4.51 ± 0.07	7 4	1.64 ± 0.26	1.11	0.02	0.08	0.03	1.01	0.04	0.11	0.08
subsample 1	4.5			1.13	0.01	0.09	0.01	0.97	0.01	0.05	0.02
subsample 2	4.45			1.11	0.02	0.06	0.04	1.02	0.03	0.18	0.06
subsample 3	4.58			1.10	0.01	0.10	0.02	1.05	0.02	0.10	0.40
	TT	or creat		\$199/198 TT ~		\$200/198 TL ~		\$201/19811~		\$202/19811~	
	н	g amt (µg)	fraction	0133/138Hg (‰)	STD	0200/138Hg (‰)	STD	0201/198Hg (‰)	STD	0 ^{202/130} Hg (‰)	STD
Hg(OH) ₂ sample	ed	20	0.1	-0.63	0.04	-1.17	0.05	-1.8	0.06	-2.43	0.05
Hg in the MQ		180	0.9	0.07	0.04	0.13	0.04	0.2	0.05	0.27	0.05
Hg(Cl) ₂ sample	d	40	0.2	0.4	0.04	0.84	0.03	1.2	0.04	1.64	0.04
Hg in the 0.01 N	I HCl	160	0.8	-0.1	0.04	-0.21	0.05	-0.3	0.06	-0.41	0.06

Other samples reported in Table 4 include synthetic solutions of Hg. These solutions were used in experiments on octanolwater partitioning of Hg species designed to assess isotope fractionation of Hg between different chemical species of the element. Two series of experiments were performed. The first one was conducted without addition of any complexing agents to the aqueous Hg solution. The second one involved addition of HCl at concentration of 0.01 M as a complexing agent. It is known from previous studies³⁹⁻⁴⁴ that uncharged, lipophilic chemical species of Hg are strongly partitioned into octanol, while charged species remain in the aqueous phase. The experiments include mixing of 10 mL of aqueous phase with 1-2 mL of octanol. The aqueous phase is represented by 10 mL of $20 \,\mu g \, mL^{-1} \, Hg$ solution in either MQ or 0.01 M HCl adjusted to pH of 3.0-3.5 using dropwise addition of HNO₃ and NaOH. The mixture was agitated for 24 h before separating the octanol. For determination of the

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concentration and isotopic composition of Hg partitioned into octanol, back-extraction was performed using a solution of 0.15% L-cysteine/0.06 M HCl. The aqueous phase was passed through Water Oasis extraction cartridges (Waters Corp., Milford, MA) to remove traces of octanol. Then Hg remaining in the aqueous phase was separated from matrix using the anion-exchange procedure. A significant fraction of aqueous Hg species under these conditions is presented by uncharged Hg(OH)₂⁰ and Hg-(Cl)₂⁰ species; the latter occurs in solutions with the presence of chloride anion.^{39,40}

As seen from Table 4, the isotopic composition of Hg species partitioned into octanol differs from the bulk value. In the presence of HCl as a complexing agent, Hg(Cl)₂⁰ complexes presumably partitioned into octanol have an isotopic composition enriched in heavy isotopes of Hg by $0.4 \pm 0.04\%$ in terms of $\delta^{199/198}$ Hg relative to the bulk Hg. By contrast, in those experiments conducted without complexing agents in the aqueous solution, Hg(OH)₂⁰ complexes presumably partitioned into octanol have an isotopic composition depleted in heavy isotopes of Hg by $-0.63 \pm 0.04\%$ in terms of $\delta^{199/198}$ Hg relative to the bulk Hg. These data indicate that isotopic fractionation occurs between different chemical species of Hg in solution. Such species-specific isotope fractionation is of great importance for interpreting Hg isotope signatures and needs to be studied in more detail.

CONCLUSION

The proposed chromatographic separation procedure provides quantitative recovery of Hg from digested sediment samples without inducing artificial fractionation (Figure 1). The combination of anion-exchange separation and solution nebulization MC-ICPMS allows four Hg isotope ratios, ¹⁹⁹Hg/¹⁹⁸Hg, ²⁰⁰Hg/¹⁹⁸Hg, ²⁰¹Hg/¹⁹⁸Hg, and ²⁰²Hg/¹⁹⁸Hg, to be determined for sediment samples with an external reproducibility of 0.06-0.18% (2 σ) for complete procedural replicates. Three-isotope plots show that all data for sediment samples and synthetic Hg solutions define single mass fractionation lines with slopes in agreement with theoretical expectations. This consistency of measured isotope ratios, while not absolute proof of accuracy, at least demonstrates that systematic errors originating from uncorrected spectral interferences are absent. Isotope data obtained from octanol–water partitioning experiments suggest that this technique can be a useful tool for evaluation of species-specific isotope effects for Hg in natural waters.

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